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<p>(54) Title: PROCESS FOR THE PREPARATION OF OCTENES</p> <p>(57) Abstract</p> <p>A mixture of isomeric octenes having an average of 1.6 to 2.0 side chain methyl groups per molecule is prepared by dimerizing of n-butene by contact with a nickel oxide catalyst on a silica-alumina support at a temperature above 150 °C at a liquid hourly weight feed rate from 0.4 to 1.8 h⁻¹.</p>		

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PROCESS FOR THE PREPARATION OF OCTENES

This invention relates to the production of octenes by dimerizing of butenes.

Octenes are useful for conversion by the oxo alcohol process into the corresponding nonyl alcohols which are used

5 inter alia in the manufacture of plasticisers, lubricating oil additives, detergents and defoamers. For this purpose, mixtures of isomeric octenes are customarily used but it is important that the mixture shall contain a blend of isomers giving rise to the desired properties in the final product.

10 It is convenient to measure the proportions of the various isomers which are present by giving the average number of side chain methyl groups per molecule in the mixture. n-Octenes, for example, contain no side chain methyl groups, methyl-heptenes contain 1 side chain methyl group; dimethyl-

15 hexenes contain 2 side chain methyl groups; and trimethyl-pentenes contain 3 side chain methyl groups. A mixture of isomeric octenes having an average of 1.6 to 2.0 side chain methyl groups per molecule is widely regarded as especially suitable for conversion into nonyl alcohols for use in

20 plasticisers.

It is known to dimerize olefins by contact with a nickel oxide catalyst at elevated temperature. For example, United States Patent No. 3649710 (Neal et al) describes a process in which butene and propylene are first pre-treated

25 and then co-dimerized by passing over a nickel oxide

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catalyst. It is said that the pre-treatment of the olefin feed substantially improves the life of the catalyst. The co-dimerizing is effective at a temperature in the range of 175 to 250°F under pressures of 30 to 50 atmospheres. The advantage of the process is stated to be that the processing techniques described produce an acceptable butene feed free of catalyst poisons which would rapidly deactivate the catalyst if not removed. United States Patent No. 3658935 (Pine) describes a process for dimerising or co-dimerising an impure feed mixture containing n-butene propylene or mixtures thereof contaminated with impurities by passage over a nickel oxide catalyst. Hydrogen is added to the feed to lengthen the life of the nickel oxide catalyst and improve the proportion of desired dimers in the product. The co-dimerizing is conducted at 140 to 300°F under a pressure from about 150 psi to 1000 psi. These references illustrate that it has long been known that nickel oxide catalysts used in the dimerizing of olefins are liable to be deactivated by poisons present in the olefin feed.

British Specification No. 1069296 discloses the production of dimers from olefins such as butene by contact with a catalyst containing aluminum and nickel ions on a silica support at temperatures up to 400°C. British Specification No. 1215943 discloses the dimerizing of olefins including butenes by contact with the same kind of catalyst which is activated in a slightly different manner. The

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catalyst used in these specifications differs from those used in the two United States Patents referred to above, and in the present invention, by including only a small proportion of nickel and aluminum.

5 East German Specification No. 1060037 describes inter alia the dimerizing of a mixture of butenes over a catalyst based on amorphous alumina silicate containing a small proportion of nickel oxide. The operating temperature was only about 100°C, but temperatures as high as 180°C are
10 disclosed with other olefin starting materials.

Such known methods for dimerising butene to octenes suffer from one or more disadvantages, e.g. the blend of isomeric octenes obtained does not give the desired properties in the nonyl alcohols or their derivatives; the
15 total conversion of butene into octene per pass over the catalyst used is too low (e.g. less than 50 per cent); and the nickel oxide catalyst is susceptible to the presence of poisons such as oxygenated compounds or organic sulphur and nitrogen compounds, in the butene feed. Such poisons are
20 often difficult to avoid unless expensive purification procedures are used.

The present invention provides an improved process for the production of a mixture of isomeric octenes having an average of 1.6 to 2.0 side chain methyl groups per molecule.
25 The new process gives a high conversion rate per pass. While it can be operated with pure or substantially pure butene

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feed, it can also be used with feeds of typical commercial purity and, with only slight modification, with feeds containing appreciable amounts of sulphur-containing catalyst poisons.

- 5 ~~According to the present invention, a mixture of~~
isomeric octenes having an average of 1.6 to 2.0 side chain methyl groups per molecule and containing not more than 8 per cent by weight of octenes having 3 side chain methyl groups per molecule is made by a process which comprises contacting
10 an n-butene, for example in the form of a mixture containing at least 20 per cent by weight of an isomeric mixture of n-butenes and not more than 80 per cent by weight of saturated hydrocarbons, and preferably not more than 1.5 per cent by weight of isobutene, at a temperature between about 150°C and
15 275°C and in the supercritical state with a nickel oxide (NiO) catalyst containing 5 to 30 per cent by weight, preferably 20 to 30 per cent by weight, of NiO on a silica-alumina support containing 10 to 45 per cent by weight of Al₂O₃ and having at least a surface area of 100 m²/g,
20 preferably between 100 to 450 m²/g at a liquid hourly weight feed rate of the said butene over the said catalyst being 0.4 to 1.8 h⁻¹, preferably between 0.6 and 0.7 h⁻¹.

It has been found that by operating under conditions such that the butene is contacted with the catalyst at a
25 temperature above 150° C, the possible presence of oxygen or nitrogen containing compounds in the butene feed does not affect the activity or life of the catalyst. Moreover, the

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conversion rate is not affected and the selectivity of the process for the desired octene mixture is not substantially affected.

For example if an n-butene feed containing 970 ppmw of t-butyl alcohol and 250 ppmw of water is dimerized at 80 to 100°C, the catalyst only has a life of less than 3 days corresponding to a weight ratio of product to catalyst of up to about 20. Under the conditions of the present invention, however, using the said feed and catalyst, the weight ratio of product to catalyst rises to over 600.

The catalyst can tolerate, under the specified operating conditions, the presence of small amounts of sulphur-containing compounds, such as organic sulphides or thiophenes, e.g. 1 to 40 ppmw, and preferably less than 20 or more preferably less than 10 ppmw in the butene feed without substantial deactivation over several days of operation.

Surprisingly, however, it has been found that the new process can be operated even with butene feeds containing larger amounts of sulphur provided that a small amount of a nitrogen-containing compound is present in, or is added to, the feed. The presence of such nitrogen-containing compound apparently prevents the sulphur in the feed from binding to the nickel oxide and deactivating it. According, therefore, to a feature of the invention, when the butene feed contains from 20 to 200 ppm, especially 20 to 40 ppm, of sulphur, the effect of such sulphur is counteracted by adding to the

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butene feed from 50 to 2000 ppm of a nitrogen-containing organic compound.

n-Butenes suitable for use in the present invention are commercially available from petroleum refinery operations. As already noted, such butenes should not contain more than 1.5% of isobutenes, because isobutene tends to form products with a high degree of branching. Preferably the butenes consist substantially entirely of 1-butene, cis-2-butene and/or trans-2-butene. The presence of fully saturated hydrocarbons in the feed is not in general detrimental, but if the proportion rises above about 80 per cent by weight the process becomes uneconomic. The presence of olefins containing more than 4 carbon atoms per molecule should likewise be avoided because they reduce the selectivity of the reaction to produce octenes.

The nickel oxide on silica-alumina catalyst used in the present invention is known and has been described in, for example, United States Patent 2581228. It may be made by treating a calcined silica-alumina gel with a solution of a water-soluble nickel salt, and then with an agent to precipitate the nickel on the gel, e.g. as the hydroxide or carbonate. The silica-alumina gel with the nickel hydroxide or carbonate precipitated thereon is then filtered off and dried and calcined. The proportion of NiO is chosen to provide essentially what is equivalent to a monolayer of the NiO on the silica-alumina support. Smaller or larger amounts of NiO reduce

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catalyst activity. The proportion of alumina is chosen to provide a high conversion rate combined with acceptable catalyst life. Too little alumina allows rapid catalyst deactivation, while too much gives poor conversion rates. It has been found that the temperature of the calcination not only affects catalyst life but also can dramatically affect the isomer distribution in the mixture of octenes obtained in the new process. Preferably the catalyst is calcined at 500 to 700°C so that a mixture containing a large proportion of octenes having an average of 1.6 to 2.0 side chain methyl groups per molecule is obtained.

The reaction temperature must be at least 150° C in order to achieve the required conversion rate and average number of methyl groups per molecule. However, if the temperature is too high, the proportion of side chain methyl groups increase, and it is therefore desirable to use a reaction temperature below about 275° C. Preferably, the contact temperature is in the range of 175 to 225° C, and it is especially preferred to operate at a temperature in the range of 180 to 200° C. The pressure in the reaction zone must be sufficient to keep the butenes in the supercritical state at the operating temperature. In practice this requires a pressure in the range of about 50 to 200 bars, preferably about 70 bars.

As already indicated, the feed rate of the octene mixture should be such as to ensure a liquid hourly weight

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feed rate from 0.4 to 1.8, preferably 0.6 to 0.7 h⁻¹. Above this feed rate the butene conversion falls to unacceptable levels and the number of side chain methyl groups per octene molecule falls below 1.6.

- 5 As already noted, when the butene feed contains more than about 5 ppm of sulphur, derived from mercaptans, disulphides, hydrogen sulphide and the like, the poisoning effect of the sulphur can be counteracted by adding to the feed from 50 to 2,000 ppm of a nitrogen-containing compound.
- 10 Suitable nitrogen-containing compounds are aliphatic and saturated heterocyclic primary, secondary and tertiary amines containing 1 to 12 carbon atoms, e.g. mono-, di- or tri-ethyl- amine or a saturated heterocyclic amine such as pyrrolidine. It is believed that such nitrogen-containing
- 15 compounds are effective because they prevent the sulphur-containing poisons in the butene feed from becoming bound to the nickel oxide catalyst and deactivating it. It is surprising that the nitrogen-containing compounds have this effect because at lower temperatures than those used in the
- 20 present invention, such compounds are themselves regarded as catalyst poisons.

 The process of the present invention does not require special apparatus and can be operated in any reactor configuration which is capable of promoting intimate contact

25 between the butene feed and the catalyst. The process can be operated batchwise, semi-batchwise, or continuously. Continuous operation in a fixed bed reactor is preferred.

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Besides the desired octene mixture, the process of the present invention produces minor amounts of C₅₋₇ and C₉₋₁₆ olefins. Of these the most important are the dodecenes, which in some cases are produced in a weight proportion as high as half that of the octenes. It is usually economically worthwhile to isolate and separate such by-product olefins.

The following Examples illustrate the invention:

Examples 1-24

The butene feed in these Examples was a commercial product which contained the following major ingredients and impurities:

<u>FEED</u>		<u>IMPURITIES</u>	
iso-butane	: 4.3 wt%	1,3-butadiene	: 350 ppmw
n-butane	: 14.5	acetylenics	: <10 ppmw
15 n-butene-1	: 44.5	oxygenates (alcohols)	: < 5 ppmw
iso-butene	: 1.2	ethers	: < 5 ppmw
trans-butene-2	: 22.0	sulfur	: 2 ppmw
cis-butene-2	: 13.5	chlorine	: < 2 ppmw

20 The butene mixture was passed over a 28 weight per cent NiO catalyst on a silica-alumina support containing 75 weight per cent silica and 25 weight per cent alumina, in the form of 3 mm tablets at a temperature in the range 185 to 195° C at a liquid hourly weight feed rate of about 0.6 to 25 1.6. The pressure in the reaction zone was maintained at 70 bars.

In the Tables:

a) W.W.H. is the liquid hourly weight feed rate, in the case of the batch examples 44-61 this is defined as the

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inverse of the feed weight divided by the catalyst weight multiplied by the reaction time.

b) CATLIFE, $W_{\text{prod}}/W_{\text{cat}}$, is the length of each experimental run measured as the ratio of weight product
5 produced to weight of catalyst used.

c) Conversion is the percentage of butene feedstock reacted.

d) Selectivity is the ratio of a specific product to the amount of butene feedstock reacted.

10 e) Yield is selectivity x conversion.

"ISOMER DISTRIBUTION" is C_8 isomer distribution and "av Branchiness" is the average number of methyl groups per molecule obtained by gas chromatographic analysis of the octene product after hydrogenation.

15 The following Table shows the results of 24 experiments:

EXAMPLES 1 - 24

OLEFINS/SATURATES:81/19 wt%

EXAMPLE	1	2	3	4	5	6	7	8	9	10	11	12
T, deg C	185	185	185	185	195	195	195	195	195	195	195	195
P, bar	70	70	70	70	70	70	70	70	70	70	70	70
W.W.H.	0.99	1.00	1.00	1.52	1.55	1.56	1.57	1.54	1.65	1.62	1.60	1.60
CONVERSION, wt%	85.9	88.9	91.5	87.2	92.0	93.7	96.6	96.7	96.1	95.7	94.2	92.5
CATLIFE, wprod/wcat	16.6	33.9	51.7	51.7	79.4	79.4	167.8	196.8	196.8	227.7	257.1	257.1
SELECTIVITY, wt%	C8 50.59	47.72	42.81	46.25	33.63	32.44	28.21	27.79	29.70	29.73	35.01	38.07
YIELD, wt%	C8 43.48	42.44	39.17	40.32	30.94	30.39	27.26	26.87	28.53	28.46	32.99	35.21

ISOMER DISTRIBUTION (after hydrogenation)

Linear (wt)	2.73	1.10	0.65	0.72	0.56	0.52	0.65	0.67			0.48	
Mono-branched	14.73	11.97	11.48	11.09	13.74	13.64	15.36	15.64			13.39	
Di-Branched	77.51	81.25	82.07	82.42	79.63	79.99	78.57	78.32			80.63	
Tri-Branched	5.04	5.69	5.81	5.77	6.06	5.85	5.41	5.37			5.50	
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00			100.00	
av Branchiness	1.85	1.92	1.93	1.93	1.91	1.91	1.89	1.88			1.91	

EXAMPLES 1 - 24

OLEFINS/SATURATES: 81/19 wt%

EXAMPLE T, deg C P, bar	13 195 70	14 195 70	15 195 70	16 195 70	17 195 70	18 195 70	19 195 70	20 195 70	21 195 70	22 195 70	23 195 70	24 195 70
W.W.R	1.61	1.58	1.54	1.59	1.56	1.40	1.50	1.56	1.47	1.49	1.52	1.52
CONVERSION, wt%	91.7	91.2	89.9	89.2	88.5	88.0	87.0	85.2	84.3	83.5	84.5	86.3
CATALYST, wprod/wcat	285.9	285.9	366.9	394.6	421.6	445.6	471.1	548.7	572.9	597.2	622.1	647.6
SELECTIVITY, wt%	C8 37.82	38.12	42.32	46.59	44.74	44.65	44.66	48.04	49.04	50.74	49.03	47.85
YIELD, wt%	C8 34.67	34.76	38.05	41.54	39.58	39.30	38.86	40.92	41.36	42.35	41.43	41.28

ISOMER DISTRIBUTION (after hydrogenation)

Linear (wt)	0.34	0.32	0.30	0.16	0.24	0.00
Mono-branched	11.43	10.53	10.15	9.05	10.20	9.33
Di-Branched	82.51	83.50	83.97	85.00	83.91	84.97
Tri-Branched	5.73	5.65	5.58	5.79	5.54	5.70
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00
av Branchiness	1.94	1.94	1.95	1.95	1.95	1.95

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Examples 25 to 43

The butene feed in these Examples contained the following major ingredients and impurities:

<u>FEED</u>			<u>IMPURITIES</u>	
5	iso-butane	: 3.3 wt%	1,3-butadiene	: 4850 ppmw
	n-butane	: 36.8	acetylenics	: 50 ppmw
	n-butene-1	33.0	oxygenates (alcohols)	: 30-50 ppmw
	iso-butene	: 1.4	Me ₂ O	: 50 ppmw
10	trans-butene-2	: 15.9	Et ₂ S ₂	: 8 ppmw as S
	cis-butene-2	: 9.6	Me ₂ S	: 7 ppmw as S
			Cl	: < 2 ppmw

The mixture of n-butenes was contacted with the same catalyst as that used in Examples 1 to 24 (in the form of 3 mm tablets) at the temperatures, pressures and contact times shown in the following table:

EXAMPLES 25 - 43

OLEFINS/SATURATES:61/39 wt%

EXAMPLE	25	26	27	28	29	30	31	32	33	34	35
T, deg C	185	195	195	195	185	195	195	200	205	205	205
P, bar	70	70	70	70	70	70	70	70	70	70	70
W.W.R.	1.54	1.54	1.63	1.53	1.57	1.58	1.57	1.54	1.55	1.58	1.26
CONVERSION, wt%	45.6	82.9	82.0	80.4	57.0	77.9	75.0	80.7	83.6	81.2	87.2
CATALYST, wt%	10.1	65.3	84.5	102.1	115.0	132.6	183.3	201.2	219.9	238.3	254.8
wprod/wcat											1.4
SELECTIVITY, wt%	CB	70.64	38.44	42.09	41.48	61.78	40.50	42.84	38.70	35.91	37.49
YIELD, wt%	CB	32.22	31.86	34.51	33.37	35.22	31.54	32.13	31.24	30.01	30.44
											28.43

ISOMER DISTRIBUTION (after hydrogenation)

Linear (wt)	12.34	0.20	0.21	0.17	0.01	0.00	0.00	0.00	0.00	0.16	0.24
Mono-branched	37.78	8.86	8.51	8.31	6.18	7.56	8.00	6.64	6.64	10.04	10.60
Di-branched	44.05	84.87	85.21	85.55	88.56	86.13	85.17	85.89	85.89	83.02	81.93
Tri-branched	5.83	6.07	6.08	5.96	5.25	6.31	6.83	7.47	7.47	6.78	7.03
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
av Branchiness	1.43	1.97	1.97	1.97	1.99	1.99	1.99	1.99	2.01	1.96	1.96

EXAMPLES 25 - 43

OLEFINS/SATURATES: 61/39 wt%

EXAMPLE	36	37	38	39	40	41	42	43
T, deg C	205	205	205	215	215	210	220	220
P, bar	70	70	70	70	70	70	70	70
W.W.R.	1.58	1.60	2.13	2.10	1.54	1.56	1.54	1.51
CONVERSION, wt%	86.1	80.5	70.5	80.9	86.4	76.42	85.99	71.25
CATALYST, wprod/wcat	254.8	312.8	335.3	335.3	355.3	373.6	393.5	474.4
SELECTIVITY wt%	C8 35.15	39.42	48.72	38.11	33.97	43.15	36.08	49.24
YIELD, wt%	C8 30.26	31.73	34.37	30.82	29.36	33.84	31.03	35.09

ISOMER DISTRIBUTION (after hydrogenation)

Linear (wt)	0.21	0.20	0.13	0.00	0.18	0.13	0.36	0.26
Mono-branched	10.86	10.10	8.85	9.77	9.48	9.38	13.34	11.75
Di-branched	82.03	83.24	84.53	82.67	82.59	83.73	79.46	81.85
Tri-branched	6.91	6.46	6.48	7.56	7.75	6.76	6.83	6.14
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
av Branchiness	1.96	1.96	1.97	1.98	1.98	1.97	1.93	1.94

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Examples 44 to 50

In a further series of experiments pure n-butene-1 was contacted with the same nickeloxide on silica-alumina catalyst at temperatures in the range 155 to 220° C and at 5 contact times from 0.67 to 1.67 per hour with the results shown in the following table:

TABLE 3

	Ex .No.	W.W.H.	Temp.°C	Percent. Conv.	Average CH ₃ /mol
	44	0.67	180	81	1.77
10	45	0.67	125	75	1.50
	46	1.00	200	81	1.71
	47	0.67	220	81	1.65
	48	1.67	220	77	1.72
	49	1.67	155	78	1.61
15	50	1.00	155	78	1.65

These results show that too low a temperature gives too low a proportion of side chain methyl per molecule.

Examples 51-57

The same procedure as in Examples 44 to 50 was repeated 20 using trans-2-butene as the starting material. The catalyst (which was the same as that used in Example 1) was crushed to 10-14 mesh particles and then calcined in an electric furnace at 500°C for 16 hours in flowing air. In a dry box, a 300 ml autoclave was loaded with the catalyst, a known weight of 25 decane used as internal standard, and (where acid) an additive (pentanethiol, pyrrolidine, diethyl disulfide). The autoclave was evacuated/N₂-purged three times, then charged

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decane used as internal standard, and (where acid) an additive (pentanethiol, pyrrolidine, diethyl disulfide). The autoclave was evacuated/ N_2 -purged three times, then charged with a known amount of high purity (>99%) butene. This step
5 was followed by heating the autoclave to the set temperature for predetermined length of time with continuous stirring. The butene/catalyst weight ratio and heating time corresponded to the space velocity indicated in Table 4 below. At the end of the run, the autoclave was cooled to
10 $\approx 5^\circ C$, vented to the air, and the liquid product was analysed by gas chromatography. The following results were obtained:

TABLE 4

Ex. No.	Poison/ wppm*	Additive/ wppm*	W.W.H.	Temp. °C	Percent Conv.	% Selectivity to		Averag CH ₃ /mo
						C ₈ =		
51	None	None	1.0	175	80	41		1.6
52	Pentanethiol 31	None	1.0	175	83	31		1.8
53	Pentanethiol 31	Pyrrolidine 500	1.0	175	81	36		1.7
54	Pentanethiol 31	Pyrrolidine 1000	1.0	175	40	40		1.7
55	None	None	1.0	155	78	42		1.7
56	diethyl disulfide 173	None	1.0	155	82	26		1.8
57	diethyl disulfide 173	Pyrrolidine 1000	1.0	155	79	35		1.8

* Weight ppm relative to the butene feed. Pentanethiol and diethyl disulfide are reported as sulfur.

These results show that the percentage selectivity for the desired octenes is reduced by the presence of sulphur-containing poisons and that this effect can be counteracted by adding nitrogen-containing compound.

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Examples 58-61

The same procedure as in Examples 44 to 50 was repeated using pure trans-2-butene as the starting material and the same catalyst as that used in Examples 51-58. The temperature and feed rate was varied as shown in the following Table which also shows the results obtained.

TABLE 5

<u>Ex. No</u>	<u>W.W.H</u>	<u>Temp, °C</u>	<u>Percent. Conv.</u>	<u>Average CH₃/mol</u>
58	1.00	175	83	1.62
59	5.00	175	58	1.43
60	1.00	95	72	1.58
61	5.00	95	44	1.39

These results show that too high a feed rate or too low an operating temperature fail to achieve the desired degree of branching of the octene product.

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CLAIMS

1. Process for the preparation of a mixture of isomeric octenes having an average of 1.6 to 2.0 side chain methyl groups per molecule and containing not more than 8 per cent
5 by weight of octenes having 3 side chain methyl groups per molecule which comprises contacting an n-butene at a temperature between about 150° and 275°C and in the supercritical state with a nickel oxide (NiO) catalyst containing 5 to 30 per cent by weight of NiO, on a silica-
10 alumina support containing 10 to 45 per cent by weight of Al₂O₃ and having at least a surface area of 100 m²/g, at a liquid hourly weight feed rate of the said butene over the said catalyst of 0.4 to 1.8
h⁻¹.
- 15 2. Process according to claim 1 in which said n-butene is present in a mixture containing at least 20 per cent by weight of butenes and not more than 80 per cent by weight of saturated hydrocarbons.
3. Process according to claim 2 in which said mixture
20 contains not more than 1.5 weight per cent of isobutene.
4. Process according to any one of claims 1 to 3 in which the n-butene contains 1 to 40 ppm of sulphur.
5. Process according to any one of claims 1 to 3 in which the n-butene contains from 40 to 200 ppm of sulphur,
25 and from 50 to 2,000 ppm of an organic nitrogen-containing compound is added to the n-butene.
6. Process according to any one of claims 1 to 4 wherein the said catalyst contains 20 to 30 per cent by weight of NiO

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of NiO and the surface area of the support is 100-450 m²/g.

7. Process according to any one of claims 1 to 6 in which the said liquid hourly weight feed rate is 0.6 to 0.7 h⁻¹.


5 8. Process according to any one of claims 1 to 7 in which the said contact takes place at a temperature in the range 175 to 225° C.

9. Process according to any one of claims 1 to 8 in which the said nickel oxide catalyst on the silica-alumina
10 support has been activated by calcination at a temperature of 500° to 700° C before use.

10. Process according to any one of claims 1 to 9 wherein the contact takes place at a pressure of 50 to 200 bars.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/02011

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 07 C 11/02, C 07 C 2/10, B 01 J 23/74		
II. FIELDS SEARCHED Minimum Documentation Searched ? Classification System Classification Symbols IPC ⁵ C 07 C 2/00 Documentation Searched other than Minimum Documentation. to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁸		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 2642467 (J.P. HOGAN) 16 June 1953 ---	
A	US, A, 3658935 (L.A. PINE) 25 April 1972 (cited in the application) -----	
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 25th March 1991		Date of Mailing of this International Search Report 03.05.91
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer 

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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9002011
SA 43079

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 2642467		None	
US-A- 3658935	25-04-72	None	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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